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A new furan annelation reaction by the palladium-catalyzed reaction of 2-alkynyl carbonates or 2-(1-alkynyl)oxiranes with β-keto esters

Ichiro Minami, Masami Yuhara, Hiroyuki Watanabe, and Jiro Tsuji*
Tokyo Institute of Technology, Meguro, Tokyo 152 (Japan)
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Abstract

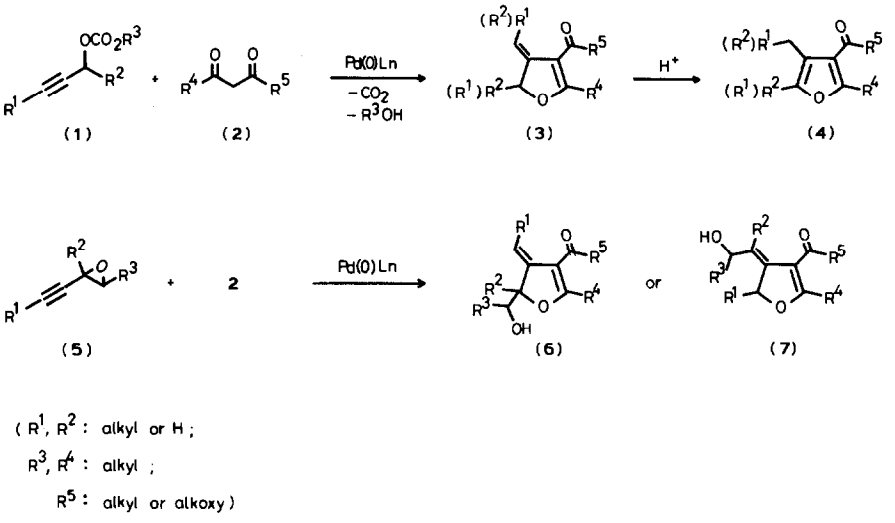
A new furan annelation by the palladium-catalyzed reaction of 2-alkynyl carbonates with β-keto esters is described. The reaction proceeds under mild neutral conditions and hence unstable 3-alkylidene-2,3-dihydrofurans can be prepared in this way. Similarly, reaction of 2-(1-alkynyl)oxiranes with β-keto esters gives alkylidene furans.

Introduction

It is well known that 2-propynyl halides, alcohols, and their derivatives react with organocopper reagents to give substituted allenes [1]. Furthermore, organomagnesium or zinc reagents react with 2-propynyl compounds in the presence of a palladium [2], copper [3], or nickel [4] catalyst. However, no examples of reactions with soft carbonucleophiles catalyzed by transition metal complexes have been reported.

In our continuing work on the palladium-catalyzed reaction of allylic compounds, we have found that allylic carbonates are very reactive compounds in palladium-catalyzed organic reactions, such as allylation of carbonucleophiles [5], dehydrogenation of alcohols [6], and preparation of α,β-unsaturated ketones, aldehydes, or esters [7], under neutral conditions. In view of the facile reactions of allylic carbonates, we expected that 2-alkynyl carbonates (**1**) to have high reactivities in the palladium-catalyzed reactions. In the course of our studies on the palladium-catalyzed reaction of carbonates, we have found that compounds **1** react with β-keto esters having one active proton, or malonates to give 2,3-disubstituted propenes. Furthermore, we have found that compounds **1** react with β-keto esters or β-diketones (**2**) bearing two active protons to give 3-alkylidene-2,3-dihydrofurans (**3**) by the catalysis of Pd^0-phosphine complexes.

2-(1-Alkenyl)oxiranes are other reactive substrates in the palladium-catalyzed reactions [8] and react with soft carbonucleophiles under neutral conditions [9].



(R^1, R^2 : alkyl or H ;
R^3, R^4 : alkyl ;
R^5 : alkyl or alkoxy)

SCHEME 1

Similarly we have found that 2-(1-alkynyl)oxiranes (**5**) react with β-keto esters (**2**) to give 3-alkylidene-2,3-dihydrofurans (**6** or **7**). Part of these studies has been reported previously [10], and details of the reaction are presented in this paper.

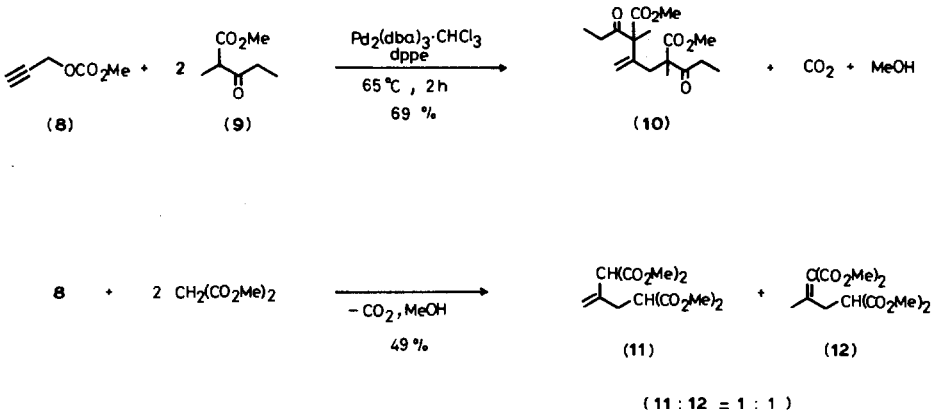
Results and discussion

Reaction of 2-alkynyl carbonates

We have found that β-keto esters having one active proton such as **9** react with methyl 2-propynyl carbonate (**8**) in a 2:1 ratio in the presence of $Pd_2(dba)_3 \cdot CHCl_3$-dppe catalyst in boiling THF for 2 h to give 2,3-disubstituted propene (**10**). In other words, two nucleophiles are introduced into the propargyl carbonate (**8**). In this case, both nucleophiles react at their carbons and no O-alkylation was observed. Dimethyl malonate reacts with **8** in boiling THF for 2 h to give the adducts **11** and **12** in 49% yield. After boiling in dioxane for 9 h, the *exo*-double bond of **11** isomerized almost completely to the stable conjugated position to give **12** in 69% yield.

Methyl acetoacetate (**13**) behaved differently from **9** and dimethyl malonate, reacting with **8** at 20–25 °C in a 1:1 molar ratio. The product was dramatically different from those of the reactions depicted in Scheme 2. Careful studies of ^1H and ^{13}C NMR spectra of the product revealed that it is neither a simply substituted propene, allene, nor an acetylene derivative, but a furan derivative which must be either **15** or **15′**.

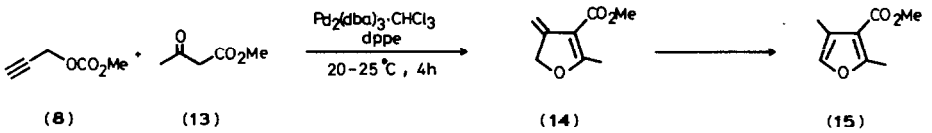
To confirm the structure of the furan, we prepared authentic samples of the substituted furans, **15** and **15′**, by standard methods. Alkylation of **13** with 2-propynyl bromide gave **15** [11], and dehydration of methyl 2-(1-oxoethyl)-4-oxopentanoate with polyphosphoric acid trimethylsilyl ester [12] gave **15′**. Careful comparative studies of NMR and IR spectra of the product with those of the authentic samples **15** and **15′** revealed that the product was **15**. Furthermore, we



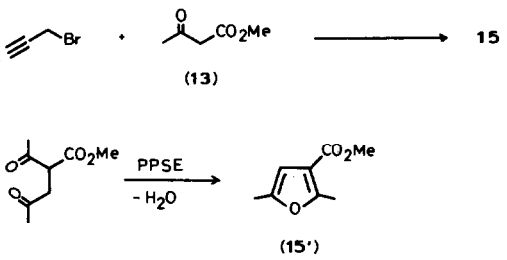
SCHEME 2

have found that the primary product of the palladium-catalyzed reaction is 4-methoxycarbonyl-5-methyl-3-methylene-2,3-dihydrofuran (**14**), which readily isomerizes to the stable furan, **15**. The methylene furan, **14**, was isolated by column chromatography on alumina or silica gel (Merck). Column chromatography on acidic silica gel (Kanto, for details, see Experimental) gave the furan, **15**, and a small amount of **14**. The results indicate that the exomethylene furan **14** underwent smooth isomerization under slightly acidic conditions. In fact, pure **14**, isolated by column chromatography on alumina, was isomerized to **15** by passing it through a short silica gel column. The isomerization took place quantitatively by treatment with HCl at 20–25 °C for 10 min.

(Continued on p. 230)



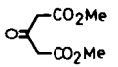
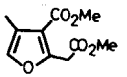
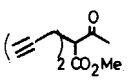
SCHEME 3. Preparation of the authentic samples.

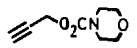
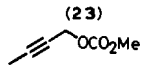
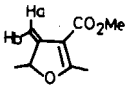
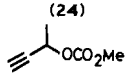
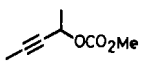
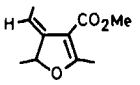
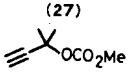
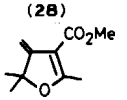
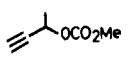
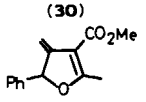


SCHEME 3

TABLE 1

REACTION OF 2-ALKYNYL COMPOUNDS [a]

Run	Carbonate	Nucleophile	Temp (°C)	Time (h)	Product	Yield (%)
1	**8**	 (16)	60	1	 (17)	77 [b]
2	**8**	 (18)	80	2	 (19)	86 [b]
3	**8**	 (20)	80	4	 **21**	39 [b]
4 [c,d]		**13**	80	2	**14**	76
5 [c,d]		**13**	80	4	**14**	20
					 (22)	44

6	 (23)	**13**	25–30	21	**14**	70
7	 (24)	**13**	60	1	 (25)	97
8	 (26)	**9**	60	1	**25**	79
9	 (27)	**13**	60	0.5	 (28)	94
10	 (29)	**13**	60	1	 (30)	97
11	 (31)	**13**	60	1	 (32)	80

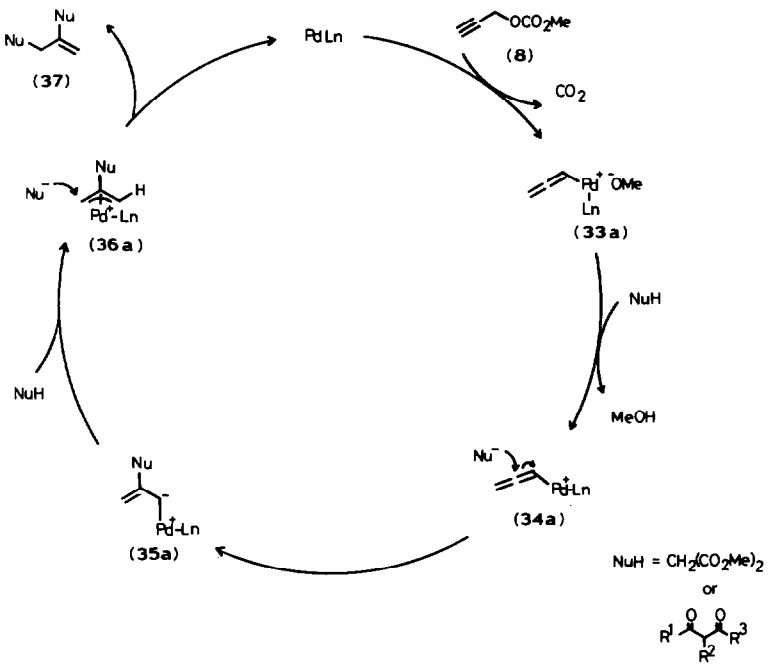
[a] Reactions were carried out using 2-alkynyl carbonate (2 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (0.1 mmol), dppe (0.2 mmol) in THF under argon. [b] Yield after treatment with 3 *N* HCl at 25–30 °C for 10 min. [c] Reaction was carried out in dioxane. [d] NaH (1 mmol) was added.

Reactions of 2-alkynyl carbonates with several carbonucleophiles were carried out. As shown in Table 1, β-keto esters and β-diketones bearing two active hydrogens are reactive nucleophiles for the furan annelation. They react with 2-alkynyl carbonates in a 1 : 1 molar ratio. Both C- and O-alkylations took place in these compounds to give 3-methylene-2,3-dihydrofurans. Various active methylene compounds such as acetylacetone (**16**), dimethyl 3-oxoglutarate (**18**) and 1,3-cyclohexanedione (**20**) showed similar reactions with **8**, to give the corresponding furans, **17**, **19**, and **21** respectively.

The smooth cyclization proceeded under completely neutral conditions with methyl 2-propynyl carbonate (**8**) or 2-propynyl carbamate (**23**), although the latter is slightly less reactive. On the other hand, addition of a base is necessary for the reaction of 2-propynyl acetate (76%) and bromide (20%) (runs 4 and 5). However, in the latter reaction, a simple substitution reaction took place to give **22** predominantly.

The stereochemistry of the *exo*-double bond was studied by comparing ^{1}H NMR spectra of **25** and **28**. The olefinic protons of **25** appear at δ 4.59 (H_b) and 5.38 (H_a) ppm. The proton, H_a, lying *cis* in the plane of the ester carbonyl group resonates downfield from the *trans* proton, H_b. Examples of the deshielding of *cis*-γ-protons with carbonyl function have been reported [13]. The olefinic proton of **28** appears at δ 5.02 ppm. Appearance of the vinylic proton of **28**, 0.43 ppm downfield from H_b in **25**, indicates that the double bond in **28** is *E*-form [14]. This conclusion is also in agreement with the mechanistic consideration that the *E*-double bond should be formed from the more stable *syn*-(π-allyl)palladium intermediate rather than the *anti* form (see Scheme 5).

In order to explain these results, we propose the following mechanisms. Scheme 4 shows the mechanism of the formation of the 2,3-disubstituted propenes (**37**). The initial step is S_N2' reaction of the palladium-phosphine complex with **8** and subsequent decarboxylation to give the (1,2-propadienyl)palladium methoxide complex **33a**. (Formation of the (1,2-propadienyl)palladium complex by the oxidative addition of the Pd^0 species to 2-propynyl acetate has been reported [15]. Moreover, formation of the complex **33a** was assumed to be the intermediate in other palladium-catalyzed reactions of 2-alkynyl carbonates (**1**) such as hydrogenolysis with ammonium formate [16] and carbonylation [17].) The methoxide anion then captures an acidic hydrogen from the nucleophile to give the complex **34a**. Next, the carbanion of the nucleophile attacks the C(2)-carbon of the 1,2-propadienyl moiety to form the palladium carbene complex, **35a**, which picks up active hydrogen from another nucleophile to give the (π-allyl)palladium complex, **36a**. Finally, the well-known nucleophilic substitution of the (π-allyl)palladium complex, **36a** [18] takes place to give the 2,3-disubstituted propene **37**. Recently, formation of the palladium carbene complexes by desilylation of α-(1-trimethylsilylallyl)palladium complexes and subsequent reaction with carbonucleophiles have been reported [19]. It is known that the palladium-catalyzed reaction of propargyl acetate with hard carbonucleophiles such as alkyl-zinc or -magnesium compounds gives alkyl 1,2-propadienyl palladium complexes, which undergo reductive elimination to afford alkylated 1,2-dienyl compounds [2,15]. On the other hand, in the reaction of soft carbonucleophiles reported here, the nucleophile first attacks the central *sp*-carbon of the (1,2-propadienyl)palladium complex selectively. No example of such a reaction with alkenyl palladium complexes is known.



SCHEME 4

The mechanism of the furan annelation is shown in Scheme 5. The difference in the mechanism of 2,3-disubstituted propene formation and that of furan annelation is in the second step of the nucleophilic substitution reaction. In the former case, the second nucleophilic substitution takes place intermolecularly. On the other hand, in the latter reaction, intramolecular O-allylation leads to the formation of 3-alkylidene-2,3-dihydrofurans.

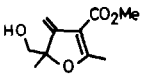
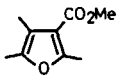
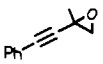
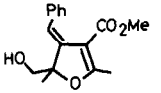
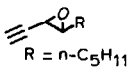
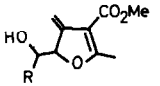
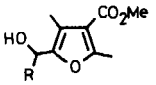
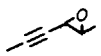
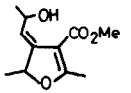
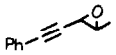
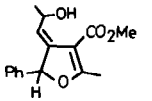
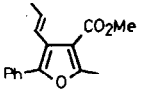
In order to study the details of the mechanism, reaction of **24** was carried out with a labelled reagent (methyl 2,2-bisdeuterioacetoacetate (**13′**)), and 2-deuterio-3-hydrofuran (**38**) was obtained as a sole product. However, reaction of **26** with **13′** afforded a furan **40** which had been deuterated at the methylene carbon (1 : 1 mixture of *E* and *Z* forms). One deuterium from **13′** was transferred to different carbons in **38** or **40**. These results clearly show that the oxidative addition of 2-alkynyl carbonate to a Pd^0 species proceeds by S_N2' reaction.

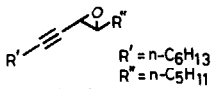
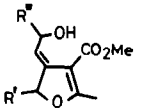
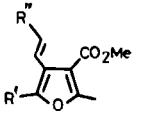
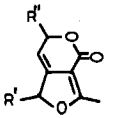
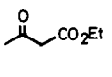
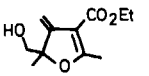
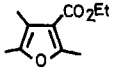
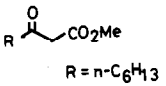
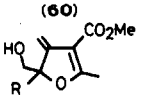
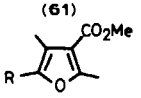
The fact that reaction of isomeric carbonates, **24** or **26**, with **13** to give the same product, **25**, shows that the furan annelation proceeds via the common (π-allyl)palladium intermediate (Table 1 runs 7 and 8). It is noteworthy that no ethylidene furan such as **39** was obtained in this reaction. The results indicate that the second nucleophilic substitution (O-allylation) occurred where the (π-allyl)palladium intermediates **36b** or **36b′** are more substituted. The same tendency was observed in the reaction of **29** and **31**. Surprisingly, for **29** the second O-allylation took place at the tertiary carbon rather than at the primary carbon. These results are in sharp contrast to usual nucleophilic substitutions in the (π-allyl)palladium complex, which occur on the less-substituted side [18]. The results may be due to steric hindrance of intermediate **36b′**.

(Continued on p. 234)

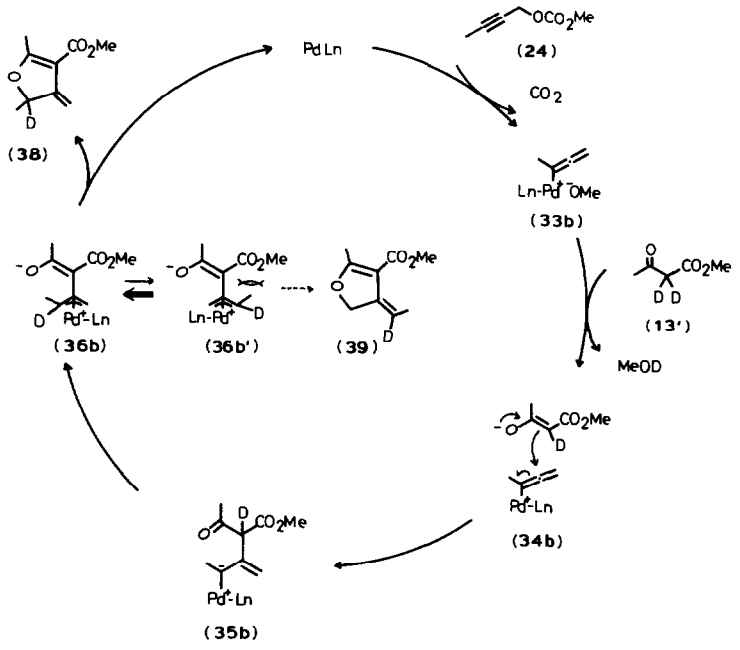
TABLE 2

REACTION OF 2-(1-ALKYNYL)OXIRANES WITH β-KETO ESTERS [a]

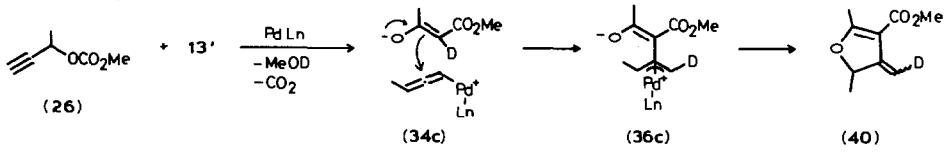
Run	α-Alkynyl epoxide	β-Keto ester	Temp (°C)	Time (h)	Primary product	Isomerized product	Yield (%)
1	 (41)	13	25–3(	2	 (42)	 (43)	75
2	 (44)	13	60	1	 (45)		82
3	 R = n-C_5H_{11} (46)	13	65	4	 (47)	 (48)	50
4	 (49)	13	50	1	 (50)	 (51)	82
5	 (52)	13	65	1	 (53)	 (54)	75

6	 R′ = n-C6H13, R″ = n-C5H11 (55)	13	25–30	3	 (56)	 (57)	53
						 (58)	8
7	**41**	 (59)	25–30	1	 (60)	 (61)	70
8	**41**	 R = n-C6H13 (62)	25–30	1	 (63)	 (64)	74

[a] Reactions were carried out using 2-(1-alkynyl)oxirane (1 mmol), β-keto ester (1 mmol), $Pd_2(dba)_3 \cdot CHCl_3$ (0.025 mmol), and dppe (0.05 mmol).



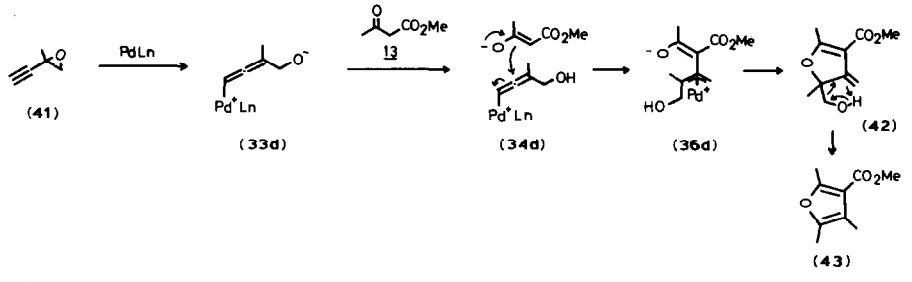
SCHEME 5



SCHEME 6

Reaction of 2-(1-alkynyl)oxiranes

We applied the palladium-catalyzed reaction to 2-(1-alkynyl)oxiranes (**5**) and collected the expected furan derivatives in good yields. The results are shown in Table 2. The substituted furans, derived from **5**, are highly unstable compounds.



SCHEME 7

They converted to stable furans even during their ^{1}H-NMR, ^{13}C-NMR, and IR analyses. Thus, spectral data of certain furans were obtained with their more stable isomers. Different furans give different conversions. For example, the exomethylene furan **42**, derived from **41** and **13**, underwent quantitative dehydroxymethylation to give **43** by acid treatment (short silica gel column), while the phenyl-substituted furan **45** underwent very little dehydroxymethylation under the same conditions. **47**, which has a tertiary carbon at C(5), the isomerization of the exomethylene double bond took place to give the furan **48** without elimination.

Only one stereoisomer due to the benzylidene double bond was obtained after reaction of **44** with **13**. As for the ethylidene furan, **28**, we concluded that the stereochemistry of the *exo*-double bond in **45** is *E*-form. Regioselectivity of the cyclization depends on the substituents, R^1–R^3. When 1,4-di-substituted-3-butyn-1,2-epoxides ($R^1 \neq H$, and $R^3 \neq H$), were allowed to react, 3-alkylidene-2,3-dihydrofurans **7** were formed rather than **6** (Scheme 1). For example, reaction of **49** with **13** gave **50**, which underwent acid-promoted lactonization to give furolactone **51**. On the other hand, the phenyl-substituted furan **53**, obtained by the reaction of **52** with **13**, underwent dehydration to give **54** without giving furolactone. Furthermore, **56** underwent dehydration to give **57** with a small amount of the lactone, **58**.

Reaction of 2-(1-alkynyl)oxiranes with other β-keto esters was also examined. For example, reaction of **41** with the β-keto esters **59** and **62** gave the furans **60** and **63**, respectively.

As for the reaction of 2-alkynyl carbonates, the furan annelation with 2-(1-alkynyl)oxiranes can be illustrated by Scheme 7. Oxidative addition of **41** to Pd^0 species affords the complex **33d**, after which proton transfer between **33d** and **13** takes place and the subsequent two-step nucleophilic substitution reaction gives the furan, **42**.

Conclusion

2-Alkynyl carbonates and 2-(1-alkynyl)oxiranes undergo smooth reaction with β-keto esters or β-diketones having two active hydrogens to give methylene furans in good yields under neutral conditions. Soft carbonucleophiles such as β-keto esters or β-diketones selectively attack the central *sp*-carbon of the (1,2-propadienyl)palladium complex. No example of such a reaction of alkenyl palladium complexes is known. Furthermore, no other route to unstable 3-alkylidene-2,3-dihydrofurans is known [20]. 3-Methylfurans, which abound in naturally occurring terpenoids [21], can be thus prepared by the methods described above.

Experimental

General

^{1}H NMR spectra were recorded on a JEOL Model FX-90Q Fourier transform spectrometer in $CDCl_3$ solution at 90 MHz relative to tetramethylsilane as internal standard. Infrared spectra were recorded on a JASCO Model IRA-2 spectrometer.

THF and dioxane were dried over $LiAlH_4$, distilled, and stored under argon. $Pd_2(dba)_3 \cdot CHCl_3$ was prepared by the published procedure [22]. 1,2-Diphenylphosphinoethane (dppe) was recrystallized from ethanol and stored under argon.

Column chromatography for isolation of alkylidene furans was performed on

activated aluminum oxide (Kanto No. 01174) or silica gel (Merck No. 10185). Use of acidic silica gel (Kanto, No. 37047) causes isomerization of the *exo*-double bond.

*Reaction of **8** with **9** (Scheme 2)*

$Pd_2(dba)_3 \cdot CHCl_3$ (52 mg, 0.1 mmol) and dppe (80 mg, 0.2 mmol) were placed in a 30 ml two-necked flask which was flushed with argon. THF (2 ml) was added and the catalyst dissolved, a solution of **8** (228 mg, 2 mmol) and **9** (288 mg, 2 mmol) in THF (3 ml) was then added and the resultant solution was stirred at 65 °C for 2 h under argon. After the reaction was complete (TLC and GLC analyses), the resultant mixture was filtered through Florisil. The product, **10**, (450 mg, 69%) was isolated by column chromatography on alumina.

*Dimethyl 2,5-dimethyl-2,5-di(1-oxopropyl)-3-methylenehexanedioate (**10**).* ^1H NMR ($CDCl_3$) δ 1.43 (s, 3H), 1.52 (s, 3H), 1.04 (t, *J* 7.2 Hz, 6H), 2.47 (q, *J* 7.2 Hz, 2H), 2.49 (q, *J* 7.2 Hz, 2H), 2.67 (br s, 3H), 3.67 (s, 3H), 3.70 (s, 3H), 4.82 (br s, 1H), 4.90 (br s, 1H). ^{13}C NMR ($CDCl_3$) δ 8.2–8.5, 18.7–18.9, 20.0, 31.4, 32.2–32.4, 36.5–36.7, 52.4, 52.6, 58.8, 66.6, 114.9–115.0, 142.4, 172.1, 173.5, 207.7, 207.8. IR (neat) 1720, 1640 cm^{-1}. Anal. Found: C, 62.72, H, 7.97. $C_{17}H_{26}O_6$ calc: C, 62.56; H, 8.03%.

Reaction of **8** with dimethyl malonate was carried out similarly. Reaction in THF at 65 °C for 2 h gave the adducts **11** and **12** in 1 : 1 ratio (GLC analysis). When the reaction was carried out in dioxane at 100 °C, **12** was isolated in 69% yield.

*Dimethyl 2,5-dimethoxycarbonyl-3-methylene-2-hexanedioate (**11**).* ^1H NMR ($CDCl_3$) δ 2.80 (d, *J* 8 Hz, 2H), 3.73 (s, 6H), 3.75 (s, 6H), 4.14 (s, 1H), 5.16 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 33.7, 50.4, 52.6, 52.7, 58.0, 118.0, 137.6, 167.8, 169.0.

*Dimethyl 2,5-dimethoxycarbonyl-3-methyl-2-hexenedioate (**12**).* ^1H NMR ($CDCl_3$) δ 2.04 (s, 3H), 3.00 (d, *J* 8 Hz, 2H), 3.75 (s, 6H), 3.77 (s, 3H), 3.78 (s, 3H), 3.64 (t, *J* 8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 21.4, 34.9, 50.1, 52.2, 52.7, 52.7, 126.5, 154.0, 165.0, 165.7, 168.9. IR (neat) 1740, 1720 cm^{-1}. Anal. Found: C, 51.95; H, 6.07. $C_{13}H_{18}O_8$ calc: C, 51.65; H, 6.00%.

General procedure for the palladium-catalyzed furan annelation

Typical procedure (Scheme 3). $Pd_2(dba)_3 \cdot CHCl_3$ (52 mg, 0.1 mmol) and dppe (1,2-diphenylphosphinoethane, 80 mg, 0.2 mmol) were placed in a 30 ml two-necked flask which was flushed with argon. THF (2 ml) was added and the catalyst was dissolved. Then a solution of **8** (228 mg, 2 mmol) and **13** (232 mg, 2 mmol) in THF (3 ml) was added and the resultant solution was stirred at 20–25 °C for 4 h under argon. After the reaction was complete (TLC analysis), the resultant mixture was filtered through Florisil. The furan **14** (271 mg, 88%) was isolated by column chromatography on alumina.

*4-Methoxycarbonyl-5-methyl-3-methylene-2,3-dihydrofuran (**14**).* ^1H NMR ($CDCl_3$) δ 2.31 (s, 3H), 3.78 (s, 3H), 4.70 (t, *J* 2.9 Hz, 1H), 5.00 (t, *J* 2.9 Hz, 2H), 5.36 (1H, t, *J* 2.9 Hz). ^{13}C NMR ($CDCl_3$) δ 15.52, 50.76, 75.89, 97.46, 106.89, 143.19, 165,25, 177.60. IR (neat) 2950, 1700, 1640, 1615, 1440, 1390, 1200, 1090 cm^{-1}.

Conversion of **14** into **15**; Several drops of 3 *N* HCl were added dropwise to a solution of **14** in THF (5 ml) and the resultant solution was stirred at 20–25 °C for 10 min. After the reaction was complete (TLC analysis), the mixture was diluted with ether, washed with saturated $NaHCO_3$ and brine. The furan **15** was isolated by column chromatography on silica gel in quantitative yield.

3-Methoxycarbonyl-2,4-dimethylfuran (15). ^{1}H NMR ($CDCl_3$) δ 2.13 (d, J 1.4 Hz, 3H), 2.52 (s, 3H), 3.82 (s, 3H), 7.02 (q, J 1.4 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 9.96, 14.25, 50.86, 113.47, 121.23, 139.77, 160.13, 165.11.

4-Acetyl-5-methyl-3-methylene-2,3-dihydrofuran. ^{1}H NMR ($CDCl_3$) δ 2.24 (s, 3H), 2.27 (s, 3H), 4.67 (t, J 3.2 Hz, 1H), 4.92 (t, J 3.2 Hz, 2H), 5.20 (t, J 3.2 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 16.37, 30.89, 75.96, 97.58, 116.36, 144.06, 177.28, 193.86. IR (neat) 2930, 1650, 1625, 1570, 1410, 1390, 1200, 1000 cm^{-1}.

3-Acetyl-2,4-dimethylfuran (17). ^{1}H NMR ($CDCl_3$) δ 2.15 (d, J 1.4 Hz, 3H), 2.40 (s, 3H), 2.52 (s, 3H), 7.02 (q, J 1.4 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 10.73, 15.22, 30.77, 120.44, 122.50, 138.00, 159.08, 194.56. IR (neat) 2950, 1660, 1590, 1550, 1410, 1265, 1110, 920 cm^{-1}.

3-Methoxycarbonyl-2-(methoxycarbonyl)methyl-4-methylfuran (19). ^{1}H NMR ($CDCl_3$) δ 2.10 (d, J 1.8 Hz, 3H), 3.70 (s, 3H), 3.81 (s, 3H), 3.98 (s, 2H), 7.07 (q, J 1.8 Hz, 1H). IR (neat) 2960, 1750, 1720, 1620, 1560, 1440, 1270, 1090 cm^{-1}.

3-Methylene-2,3,4,5,6,7-hexahydro-4H-benzofuran-4-one. ^{1}H NMR ($CDCl_3$) δ 1.98–2.46 (m, 6H), 4.75 (t, J 3.0 Hz, 1H), 4.95 (t, J 3.0 Hz, 2H), 5.59 (t, J 3.0 Hz, 1H). IR (neat) 2950, 1660, 1610, 1450, 1430, 1180, 1000, 770 cm^{-1}.

3-Methyl-4,5,6,7-tetrahydro-4H-benzofuran-4-one (21). ^{1}H NMR ($CDCl_3$) δ 2.13 (m, 2H), 2.19 (d, J 1.4 Hz, 3H), 2.47 (t, J 7.0 Hz, 2H), 2.83 (t, J 2.8 Hz, 2H), 7.06 (q, J 1.4 Hz, 1H). IR (neat) 2950, 1670, 1560, 1435, 1270, 1080, 1060, 1020 cm^{-1}.

4-Methoxycarbonyl-2,5-dimethyl-3-methylene-2,3-dihydrofuran (25). ^{1}H NMR ($CDCl_3$) δ 1.43 (d, J 6.7 Hz, 3H), 2.31 (s, 3H), 3.78 (s, 3H), 4.59 (d, J 2.8 Hz, 1H), 5.12 (t of q, J 2.8, 6.7 Hz, 1H), 5.38 (d, J 2.8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 15.62, 21.82, 50.71, 83.21, 98.00, 106.01, 148.51, 165.45, 175.55. IR (neat) 2950, 1710, 1640, 1610, 1440, 1200, 1100, 1030 cm^{-1}.

4-Methoxycarbonyl-2,5-dimethyl-3-ethylidene-2,3-dihydrofuran (28). ^{1}H NMR ($CDCl_3$) δ 1.37 (d, J 6.1 Hz, 3H), 1.74 (dd, J 2.9 and 9.7 Hz, 3H), 2.20 (s, 3H), 3.78 (s, 3H), 5.02 (m, 1H, H_a), 5.08 (m, 1H, H_b). ^{13}C NMR ($CDCl_3$) δ 14.45, 15.18, 21.93, 50.86, 83.90, 106.30, 109.28, 139.63, 165.89, 172.72. IR (neat) 2950, 1710, 1610, 1440, 1180, 1100, 1050, 990 cm^{-1}.

4-Methoxycarbonyl-2,2,5-trimethyl-3-methylene-2,3-dihydrofuran (30). ^{1}H NMR ($CDCl_3$) δ 1.34 (s, 6H), 2.32 (s, 3H), 3.78 (s, 3H), 4.50 (s, 1H), 5.36 (s, 1H). ^{13}C NMR ($CDCl_3$) δ 15.7, 28.3, 50.7, 89.8, 97.6, 105.2, 152.1, 165.6, 173.2. IR (neat) 2970, 1710, 1635, 1610, 1440, 1390, 1200, 1080 cm^{-1}.

4-Methoxycarbonyl-5-methyl-3-methylene-2-phenyl-2,3-dihydrofuran (32). ^{1}H NMR ($CDCl_3$) δ 2.39 (s, 3H), 3.79 (s, 3H), 4.53 (d, J 2.9 Hz, 1H), 2.52 (s, J 2.9 Hz, 1H), 5.94 (t, J 2.9 Hz, 1H), 7.34 (bs, 5H).

3-Methoxycarbonyl-2,4-dimethyl-5-phenylfuran. ^{1}H NMR ($CDCl_3$) δ 2.40 (s, 3H), 2.62 (s, 3H), 3.86 (s, 3H), 7.28–7.70 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 10.9, 14.4, 51.0, 115.2, 116.8, 126.1, 127.2, 128.5, 131.0, 147.8, 158.5, 165.2. IR (neat) 2940, 1710, 1610, 1495, 1440, 1240, 1095, 1020 cm^{-1}. Hi-mass (m/e) = 230.0960.

2,5-Dimethyl-4-methoxycarbonyl-3-methylene-2-deuterio-3-hydrofuran (38). ^{1}H NMR (CCl_4) δ 1.48 (t, J 4 Hz, 3H), 1.27 (s, 3H), 3.72 (s, 3H), 4.54 (bs, 1H), 5.33 (bs, 1H).

2,5-Dimethyl-3-deuteriomethylene-4-methoxycarbonyl-2,3-dihydrofuran (40). ^{1}H NMR (CCl_4) δ 1.40 (d, J 7 Hz, 3H), 2.30 (s, 3H), 3.88 (s, 3H), 4.46–4.58 (m, 0.5H), 4.82–5.27 (m, 1H), 5.30–5.38 (m, 0.5H).

3-Methoxycarbonyl-2,4,5-trimethylfuran (43). ^{1}H NMR ($CDCl_3$) δ 2.03 (s, 3H),

2.13 (s, 3H), 2.47 (s, 3H), 3.79 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 9.86, 10.93, 14.10, 50.76, 113.72, 114.70, 145.78, 157,35, 165.36. IR (neat) 2940, 1710, 1580, 1300, 1260, 1210, 1130, 1080, cm^{-1}.

3-Benzylidene-2,5-dimethyl-2-hydroxymethyl-4-methoxycarbonyl-2,3-dihydrofuran (45). ^1H NMR ($CDCl_3$) δ 1.51 (s, 3H), 1.60 (bs, 1H), 2.25 (s, 3H), 3.09 (s, 3H), 3.52–3.68 (bs, 2H), 5.91 (s, 1H), 7.00–7.30 (m, 5H). ^{13}C NMR ($CDCl_3$) δ 14.4, 22.7, 50.4, 68.7, 94.7, 107.3, 113.7, 125.9, 127.6, 127.7, 138.5, 141.2, 165.4, 172.5. IR (neat) 3450, 2970, 1700, 1620, 1500, 790, 700 cm^{-1}. Hi-mass (m/e) = 274.1222.

2,4-Dimethyl-5-(2-hydroxyhexyl)-3-methoxycarbonylfuran (48). ^1H NMR ($CDCl_3$) δ 0.78–1.04 (m, 3H), 1.04–1.50 (m, 6H), 1.70–2.04 (m, 3H), 2.14 (s, 3H), 2.52 (s, 3H), 3.81 (s, 3H), 4.65 (t, J 7.0 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 9.66, 14.10, 14.36, 22.65, 25.46, 31.66, 35.64, 51.05, 65.67, 113.9, 117.2, 149.8, 158.8, 165.3. IR (neat) 3475, 2950, 1700, 1630, 1610, 1440, 1240, 1095, 860 cm^{-1}.

2,5,7-Trimethylfuro-[4,3-c]-2',5-dihydro-3H-pyran-3-one (51). ^1H NMR ($CDCl_3$) δ 1.44 (d, J 6.4 Hz, 3H), 1.47 (d, J 6.4 Hz, 3H), 2.33 (s, 3H), 4.95–5.04 (m, 1H), 5.08–5.40 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 14.17, 20.76, 23.57, 78.85, 81.60, 100.8, 105.9, 140.9, 162.3, 171.4. IR (neat) 2940, 1705, 1640, 1280, 1060, 995, 895, 850 cm^{-1}.

3-(2-Hydroxypropylidene)-4-methoxycarbonyl-5-methyl-2-phenyl-2,3-dihydrofuran (53). ^1H NMR ($CDCl_3$) δ 1.12 (d, J 6.2 Hz, 3H), 2.31 (s, 3H), 3.10–3.40 (br, 1H), 3.83 (s, 3H), 4.50–4.88 (m, 2H), 5.91 (d, J 2.2 Hz, 1H), 7.16–7.50 (m, 5H).

3-Methoxycarbonyl-2-methyl-5-phenyl-4-(1-propenyl)furan (54). ^1H NMR ($CDCl_3$) δ 1.82 (dd, J 6.6, 1.7 Hz, 3H), 2.58 (s, 3H), 3.84 (s, 3H), 5.92 (dq, J 16.0 and 6.4 Hz, 1H), 6.48 (dq, J 16.0, 1.54 Hz, 1H), 7.29–7.50 (m, 3H), 7.60–7.76 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 14.2, 18.8, 51.1, 114.4, 121.0, 126.6, 127.4, 128.3, 130.7, 131.1, 147.5, 158.2, 164.8. IR (neat) 2950, 1720, 1610, 1330, 1225, 1100, 965, 790 cm^{-1}.

4-(1-Heptenyl)-5-hexyl-3-methoxycarbonyl-2-methylfuran (57). ^1H NMR ($CDCl_3$) δ 0.70–1.08 (m, 6H), 1.08–1.50 (m, 14H), 2.00–2.30 (m, 2H), 2.49 (s, 3H), 2.40–2.70 (m, 2H), 3.80 (s, 3H), 5.69 (dt, J 15.8 and 6.6 Hz, 1H), 6.41 (d, J 15.8 Hz, 1H). ^{13}C NMR ($CDCl_3$) δ 51.00, 112.7, 118.3, 120.8, 133.3, 150.9, 157.3, 165.3. IR (neat) 2950, 1620, 1580, 1440, 1085 cm^{-1}.

7-Heptyl-2-methyl-5-pentylfuro-[4,3-c]-2',5-dihydro-3H-pyran-3-one (58). ^1H NMR ($CDCl_3$) δ 0.70–1.08 (m, 6H), 1.08–1.75 (m, 14H), 1.75–1.85 (m, 4H), 2.33 (s, 3H), 4.85–5.00 (br, 1H), 5.00–5.24 (br, 2H). IR (neat) 2950, 1720, 1640, 1470, 1410, 1275, 1170, 1070 cm^{-1}.

4-Ethoxycarbonyl-2,5-dimethyl-2-hydroxymethyl-3-methylene-2,3-dihydrofuran (60). ^1H NMR ($CDCl_3$) δ 1.34 (t, J 7 Hz, 3H), 1.39 (s, 3H), 2.35 (s, 3H), 3.56 (d, J 6.9 Hz, 2H), 4.25 (q, J 7 Hz, 2H), 4.54 (s, 1H), 5.53 (s, 1H). IR (neat) 3450, 2960, 1690, 1605, 1380, 980, 869, 780 cm^{-1}.

3-Ethoxycarbonyl-2,4,5-trimethylfuran (61). ^1H NMR ($CDCl_3$) δ 1.34 (t, J 7 Hz, 3H), 2.05 (s, 3H), 2.16 (s, 3H), 2.49 (s, 3H), 2.27 (q, J 7 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 9.9, 10.9, 14.1, 14.3, 59.6, 113.9, 114.6, 145.7, 157.2, 165.0. IR (neat) 2970, 1710, 1640, 1210, 1080, 780, 740 cm^{-1}.

4-Methoxycarbonyl-2-hexyl-2-hydroxymethyl-5-methyl-3-methylene-2,3-dihydrofuran (63). ^1H NMR ($CDCl_3$) δ 0.88 (t, J 5.6 Hz, 3H), 1.10–1.50 (m, 8H), 1.39 (s, 3H), 2.77 (t, J 7 Hz, 2H), 3.78 (s, 3H), 4.55 (s, 1H), 5.52 (s, 1H). IR (neat) 3450, 2920, 1700, 1440, 1060, 860 cm^{-1}.

3-Methoxycarbonyl-4,5-dimethyl-2-hexylfuran (64). ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J 5.5 Hz, 3H), 1.10–1.80 (m, 8H), 2.05 (d, J 0.9 Hz, 3H), 2.16 (s, 3H), 2.89 (t, J 7.0 Hz, 2H), 3.80 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 9.9, 11.0, 14.0, 22.6, 28.1, 29.0, 31.6, 50.7, 113.2, 114.5, 145.8, 161.5, 165.4. IR (neat) 2900, 1720, 1640, 1210, 1080, 780 cm^{-1}.

Reaction of 2-propynyl acetate or bromide with 13

NaH (50% in oil, 96 mg, 2 mmol) was washed with hexane (3 ml × 3) and dioxane (3 ml) under argon, and a solution of $Pd_2(dba)_3$ $CHCl_3$ (26 mg, 0.05 mmol), dppe (40 mg, 0.1 mmol), propargyl acetate (98 mg, 1 mmol), and **13** (116 mg, 1 mmol) in dioxane (5 ml) was added and the solution stirred for 2 h at 80 °C under argon. **14** (117 mg, 76%) was then isolated by column chromatography.

Reaction of propargyl bromide was carried out similarly (80 °C, 4 h). However, base-induced alkylation took place in this reaction, giving **22**.

Preparation of materials

Preparation of 2-alkynyl carbonates

Similar procedure to that for the preparation of allylic carbonates [23].

Methyl 2-propynyl carbonate (8). Prepared from 2-propyn-1-ol and methyl chloroformate. ^{1}H NMR (CCl_4) δ 2.43 (t, J 2 Hz, 1H), 3.73 (s, 3H), 4.62 (d, J 2 Hz, 2H). IR (neat) 3300, 2950, 2130, 1750, 1445, 1270 cm^{-1}. b.p. 56 °C/18 Torr.

Methyl 2-butynyl carbonate (22). Prepared from 2-butyn-1-ol and methyl chloroformate. ^{1}H NMR (CCl_4) δ 1.82 (t, J 2 Hz, 3H), 3.70 (s, 3H), 4.53 (q, J 2 Hz, 2H). IR (neat) 2900, 2220, 1750, 1440, 1260 cm^{-1}. b.p. 84 °C/20 Torr.

Methyl 1-methyl-2-propynyl carbonate (26). Prepared from 3-butyn-2-ol and methyl chloroformate. ^{1}H NMR (CCl_4) δ 1.48 (d, J 7 Hz, 3H), 2.38 (d, J 2 Hz, 1H), 3.70 (s, 3H), 5.16 (dq, J 7 and 2 Hz, 1H). IR (neat) 3280, 2950, 2130, 1750, 1440, 1260 cm^{-1}. b.p. 57 °C/17 Torr.

Methyl 1-methyl-2-butynyl carbonate (27). Prepared from 3-pentyn-2-ol and methyl chloroformate. ^{1}H NMR (CCl_4) δ 1.43 (d, J 7 Hz, 3H), 1.80 (d, J 2 Hz, 3H), 3.69 (s, 3H), 5.13 (dq, J 2 and 7 Hz, 1H). IR (neat) 2900, 2250, 2750, 990 cm^{-1}.

1,1-Dimethyl-2-propynyl methyl carbonate (29). Prepared from 2-methyl-3-butyn-2-ol and methyl chloroformate. ^{1}H NMR (CCl_4) δ 1.50 (s, 6H), 2.41 (s, 1H), 3.60 (s, 3H). IR (neat) 3270, 2200, 1750 cm^{-1}. b.p. 63 °C/20 Torr.

Methyl 1-phenyl-2-propynyl carbonate (31). Prepared from 1-phenyl-2-propyn-1-ol and methyl chloroformate. ^{1}H NMR (CCl_4) δ 2.58 (d, J 2.5 Hz, 1H), 3.75 (s, 3H), 6.24 (d, J 2.5 Hz, 1H), 7.20–7.70 (m, 5H). IR (neat) 3280, 2950, 2125, 1750, 1260 cm^{-1}. b.p. 92 °C/2 Torr.

N-Propargyloxycarbonylmorpholine (23). Prepared from morpholine and propargyl chloroformate. ^{1}H NMR ($CDCl_3$) δ 2.47 (t, J 2.4 Hz, 1H), 3.55 (m, 8H), 4.72 (d, J 2.4 Hz, 2H). IR (neat) 3250, 1700, 1440 cm^{-1}. m.p. 41.0–41.5 °C.

Preparation of 2-(1-alkynyl)oxiranes

General procedure. To a solution of magnesium acetylide in THF [prepared from n-butylmagnesium bromide (50 mmol) and an acetylene compound (40 mmol)] [24], was added dropwise α-halo carbonyl compound (50 mmol) in THF (10 ml) at

0 °C under nitrogen. The resultant mixture was stirred for 1 h at 20–30 °C. After the reaction was complete (TLC and/or GLC analysis), the mixture was neutralized with 1 *N* HCl (ca. 50 ml) and the resultant mixture was extracted with ether/hexane. The extract was washed with brine and dried over $MgSO_4$. The corresponding halohydrin was then isolated by column chromatography on silica gel in 80–90% yields, and converted to the corresponding 2-(1-alkynyl)oxiranes by the following procedure.

To a mixture of dry methanol (15 ml) and dry ether (15 ml), was added slowly, sodium chips (345 mg, 15 mmol) at 0 °C under nitrogen. After the sodium chips had dissolved completely, the halohydrin (10 mmol) in ether (5 ml) was added dropwise at −15 °C. The reaction mixture was stirred for 1 h at 20–30 °C. After the reaction was complete (TLC analysis), the mixture was washed with cold saturated NH_4Cl and brine, and dried over $MgSO_4$. The 2-(1-alkynyl)oxiranes were then isolated by fractional distillation or column chromatography on silica gel in 60–80% yields.

*2-Ethynyl-2-methyloxirane (**41**).* Prepared from chloroacetone and acetylene. ^1H NMR (CCl_4) δ 1.45 (s, 3H), 2.12 (s, 1H), 2.50 (d, *J* 6 Hz, 1H), 2.80 (d, *J* 6 Hz, 1H). IR (neat) 3290, 2970, 2150, 1245, 880, 790 cm^{-1}. b.p. 26 °C/400 Torr.

*2-(2-Phenylethynyl)-2-methyloxirane (**44**).* Prepared from chloroacetone and phenylacetylene. ^1H NMR ($CDCl_3$) δ 1.65 (s, 3H), 2.83 (d, *J* 5.5 Hz, 1H), 3.11 (d, *J* 5.5 Hz, 1H), 7.28–7.50 (m, 5H). IR (neat) 2900, 2240, 1600, 1495, 1440, 1380, 1340 cm^{-1}.

*2-Ethynyl-3-pentyloxirane (**46**).* Prepared from 2-bromohexanal and acetylene. ^1H NMR (CCl_4) δ 0.70–1.10 (m, 3H), 1.10–1.80 (m, 8H), 2.10 (s, 1H), 3.30–3.50 (m, 2H). IR (neat) 3350, 2940, 2850, 2120, 1240, 980 cm^{-1}. b.p. 26-27 °C/1 Torr.

*2-(1-Propynyl)-3-methyloxirane (**49**).* Prepared from 2-bromopropanal and propyne. ^1H NMR ($CDCl_3$) δ 1.31 (d, *J* 4.8 Hz, 3H), 1.83 (d, *J* 1.8 Hz, 3H), 3.02–3.14 (m, 2H). IR (neat) 2950, 2240, 1380, 1330, 1165, 1020, 940, 850 cm^{-1}. b.p. 70 °C/56 Torr.

*3-Methyl-2-(2-phenylethynyl)oxirane (**52**).* Prepared from 2-bromopropanal and phenylacetylene. ^1H NMR (CCl_4) δ 1.28 (d, *J* 5.0 Hz, 3H), 2.90–3.10 (m, 2H), 7.00–7.40 (m, 5H). IR (neat) 2960, 2270, 1600, 1490, 1440, 1325, 1230 cm^{-1}.

*2-(1-Octynyl)-3-pentyloxirane (**55**).* Prepared from 1-octyne and 2-bromohexanal. ^1H NMR ($CDCl_3$) δ 0.70–1.04 (m, 6H), 1.04–1.70 (m, 18H), 2.00–2.30 (m, 1H), 2.90–3.10 (m, 1H).

Preparation of 2-bromo aldehydes

To a solution of aldehyde (120 mmol) and dioxane (4 mmol) in dry ether (300 ml), was added bromine (0.8 g, 5 mmol) at 20–30 °C. After the solution had become colorless, the mixture was cooled to −15 °C and bromine (15.2 g, 95 mmol) was added dropwise. The reaction mixture was then stirred for 1 h at 0 °C, after which the solution was nearly colorless, the solution was washed with saturated $Na_2S_2O_7$, $NaHCO_3$ and brine. The water layer was extracted with ether, and the organic layer dried over $MgSO_4$. A pure product was isolated by distillation in 50–85% yields.

2-Bromoheptanal. ^1H NMR (CCl_4) δ 0.60–1.00 (m, 3H), 1.05–1.65 (m, 6H), 1.65–2.15 (m, 2H), 3.90–4.25 (m, 1H), 9.10 (d, *J* 3 Hz, 1H). IR (neat) 2950, 2850, 1720, 1460, 1380, 720 cm^{-1}. b.p. 80–82 °C/20 Torr.

2-Bromopropanal. ^1H NMR (CCl_4) δ 1.72 (d, *J* 6.7 Hz, 3H), 4.18 (dq, *J* 6.7,

2.0, 1H), 9.30 (d, J 2.0 Hz, 1H). IR (neat) 2970, 2930, 2850, 1740, 1440, 1005 cm^{-1}. b.p. 110°C/760 Torr.

Preparation of methyl 2,2-bisdeuterioacetoacetate (13')
Prepared by the published procedure [25].

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